

JP2004172111

**FIELD OF THE INVENTION**

[0001]

This invention relates to the power plant using the liquid fuel cell and it which used the fluid as fuel.

5 **[BACKGROUND OF THE INVENTION]**

[0002]

10 In recent years, as for the rechargeable battery which is the power supply, a miniaturization and high capacity-ization are increasingly demanded with the spread of cordless apparatus, such as a laptop computer and a cellular phone. Now, an energy density is high, the rechargeable lithium-ion battery is put in practical use as a rechargeable battery which can attain a small weight saving, and demand is growing as a portable power supply. However, it has not resulted by the grade which guarantees continuous use time still sufficient in this lithium secondary battery depending on the kind of cordless apparatus used.

[0003]

15 In such a situation, an air cell, a fuel cell, etc. can be considered as an example of the cell which can meet the above-mentioned request (for example, refer to the patent documents 1 and patent documents 2.).

[0004]

An air cell is a cell which uses oxygen in the air as an active material of an anode.

20 Since it is possible to spend the great portion of cell content volume on restoration of a negative electrode, in order to make an energy density increase, it is thought that it is a suitable cell.

However, there is a problem that the alkali solution used as an electrolysis solution will react to the carbon dioxide in the air, and will deteriorate in this air cell.

[0005]

25 Although some candidates are mentioned about the fuel cell about the fuel to be used, it has various problems, respectively and a final determination is not yet made. For example, to use pure water matter as fuel, time and a huge amount of funds are required for maintenance of fuel-supply equipment of a hydrogen refuelling station etc. Since hydrogen is very light combustible gas, the handling is difficult for it, and there is a problem also in respect of safety. In reforming gasoline and  
30 taking out hydrogen, using gasoline as fuel, a reformer is needed, and there is also a problem that the efficiency of refining is not so high etc. In using methanol as fuel, When using refining methanol, and the same problem as gasoline arises and uses methanol as fuel as it is, without reforming, an output, efficiency, etc. become low and there is a problem that the quantity which penetrates an electrolyte membrane also has large methanol which is fuel.

35 [0006]

Then, sodium borohydride ( $\text{NaBH}_4$ ) has attracted attention as a new source of hydrogen fuel. Sodium

borohydride generates hydrogen with the following reaction formula.

[0007]

( \*\* 1)



- 5 In the alkaline aqueous solution, since the above-mentioned hydrolysis reaction does not occur easily, it can save boron hydride NATORIMU stably in an alkaline aqueous solution, and is expected as a new source of hydrogen fuel.

[0008]

- 10 In recent years, the alkali fuel cell which makes a charging state the cell which used the hydrogen storing metal alloy for the negative electrode with soluble metal hydride fuel, such as  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiAlH}_4$ ,  $\text{KH}$ , and  $\text{NaH}$ , is developed (for example, refer to the patent documents 3 and patent documents 4.). Fuel is supplied to a negative electrode, hydrogen occurs, and this alkali fuel cell makes a negative electrode once absorb this hydrogen, and is made to react. By carrying out absorption storage of the hydrogen at a negative electrode, hydrogen can be used for a reaction
- 15 according to a discharge rate. It is made to dissolve in fluids, such as solution, and the metal hydride which is fuel is used. Since especially  $\text{NaBH}_4$  is stable in an alkaline aqueous solution, it is made to dissolve in an alkaline aqueous solution, and it is used. When using an air pole for an anode, this alkali fuel cell can be continuously used, if even supply of fuel and oxygen is performed.

[Patent documents 1] U.S. Pat. No. 3419900 specification

- 20 [Patent documents 2] JP,60-54177,A

[Patent documents 3] JP,2002-289252,A (patent No. 3342699) gazette

[Patent documents 4] U.S. Pat. No. 5599640 specification

## DESCRIPTION OF THE INVENTION

25

### PROBLEM(S) TO BE SOLVED BY THE INVENTION

[0009]

- 30 If metal hydride solution is supplied to the above-mentioned alkali fuel cell as fuel, when the hydrogen storing metal alloy which are fuel and a negative electrode touches, even if the hydrolysis reaction of metal hydride occurs and the fuel cell has not generated electricity, the decomposition reaction of the metal hydride in fuel will continue. In this case, the hydrogen generated at the reaction of a negative electrode and metal hydride will not be used for power generation, and will consume fuel vainly. For this reason, some prepared fuel could be taken out as electric power, but it had become the cause of reducing the energy density of a fuel cell greatly.

- 35 [0010]

Here, useless consumption of fuel can be controlled by using the accessory vessel which controls

supply to the negative electrode of fuel. However, the volume of the whole fuel cell will become large by using an accessory vessel in this case. In addition, the structure of a fuel cell becomes complicated and it becomes difficult to use a fuel cell as a small portable power supply.

[0011]

- 5 On the other hand, by giving elasticity to an anode, an electrolyte layer, and a negative electrode, and collecting the hydrogen gas fuel reacting to a negative electrode and emitted between fuel and a negative electrode, only when having generated electricity, the fuel cell with which it was made for a negative electrode and fuel to contact is also considered. For example, if elasticity is given to the integrated object of an anode, an electrolyte layer, and a negative electrode and hydrogen gas is  
10 emitted, when this integrated object curves to an opposite hand with fuel, how to intercept contact with a negative electrode and fuel can be considered.

[0012]

- However, when using a hydrogen storing metal alloy for a negative electrode in a described method, it is difficult to give the elasticity which can realize the above-mentioned function to a negative  
15 electrode. In a described method, since a high pressure is applied to hydrogen gas between a negative electrode and fuel, there is a possibility that hydrogen gas may flow into the anode side. In order to prevent this, it is necessary to arrange the ion-conductive electrolyte of the shape of a film which does not penetrate gas to an electrolyte layer, and becomes a high cost. In order that the above-mentioned anode, an electrolyte, and a negative-electrode integrated object may repeat modification, a negative  
20 electrode to a catalyst bed or a hydrogen storing metal alloy is easily omitted from an anode, respectively, and there is a problem also in the endurance of an electrode.

[0013]

- This invention provides a liquid fuel cell with a high energy density by increasing absorption of hydrogen gas while inhibiting the reaction of the liquid fuel at the time of a power generation stop or  
25 low rate power generation.

[Means for Solving the Problem]

[0014]

- An anode in which a liquid fuel cell of this invention returns oxygen, and a negative electrode containing a hydrogen absorption material, including an electrolyte layer arranged between said anode  
30 and said negative electrode, and liquid fuel, when said liquid fuel oxidizes with said negative electrode, are a liquid fuel cell which a gas generates, and a gas generated from said liquid fuel is used, It has an adjustment device which adjusts a reaction for which said liquid fuel oxidizes with said negative electrode according to power generation quantity of electricity.

[0015]

- 35 A power plant of this invention is characterized by two or more power generation elements' being the power plants electrically connected by a gap or one side to be chosen from series and parallel, and at

least one of said the power generation elements being the above-mentioned liquid fuel cell.

[Effect of the Invention]

[0016]

5 This invention can provide a liquid fuel cell with a high energy density by increasing absorption of hydrogen gas while inhibiting the reaction of the liquid fuel at the time of a power generation stop or low rate power generation.

## BEST MODE OF CARRYING OUT THE INVENTION

10 [0017]

Hereafter, an embodiment of the invention is described.

[0018]

15 The anode in which one embodiment of the liquid fuel cell of this invention returns oxygen, and the negative electrode containing a hydrogen absorption material, The gas attaching part which can collect and hold the gas generated from liquid fuel is provided in the contact portion of a negative electrode and liquid fuel including the electrolyte layer arranged between an anode and a negative electrode, and the liquid fuel stores dept. which stored the liquid fuel containing metal hydride. A gas attaching part is in the state holding the gas generated from liquid fuel, and it is arranged so that liquid fuel and a negative electrode may not contact.

20 [0019]

Generating of the hydrogen which a negative electrode and liquid fuel react at the time of a power generation stop or low rate power generation, and is not used for power generation by providing the gas attaching part which can collect and hold the gas generated from liquid fuel to the contact portion of a negative electrode and liquid fuel will accumulate the hydrogen in a gas attaching part. If  
25 hydrogen is accumulated in this gas attaching part, contact with a negative electrode and liquid fuel will be intercepted by this accumulated hydrogen, and the reaction of a negative electrode and liquid fuel will stop. Useless consumption of liquid fuel can be controlled by this, and the energy density of a liquid fuel cell can be improved. When hydrogen in a gas attaching part is consumed at the time of usual power generation of a fuel cell, liquid fuel flows into this gas attaching part and a negative  
30 electrode and liquid fuel contact again, a negative electrode and liquid fuel react, hydrogen occurs, and power generation can be continued.

[0020]

35 Since the hydrogen accumulated into the gas attaching part is consumed in large quantities when there is much power generation quantity of electricity of a liquid fuel cell, the liquid fuel which flows into a gas attaching part also increases in number. Therefore, the area which a negative electrode and liquid fuel touch also increases, and hydrogen is also generated in large quantities. On the other hand, when

there is little power generation quantity of electricity, since there is little consumption of hydrogen of a gas attaching part, its liquid fuel which flows into a gas attaching part also decreases. Therefore, the area which a negative electrode and liquid fuel touch also decreases, and generating of hydrogen also decreases. That is, the reaction of a negative electrode and liquid fuel can be adjusted according to power generation quantity of electricity.

[0021]

If it is the structure where the generated gas can be held on the surface by the side of the liquid fuel of a negative electrode while having an opening into which liquid fuel flows as a structure of a gas attaching part, the kind in particular will not be limited. For example, the function of a gas attaching part can be demonstrated by the structure which forms an accumulating part by a diaphragm between a liquid fuel stores dept. and a negative electrode so that the hydrogen gas emitted on the surface by the side of the liquid fuel of a negative electrode can be collected.

[0022]

Since the gas generated irrespective of the installation direction of a fuel cell by making a gas attaching part into pipe shape, and considering the installation direction of the tubular part as the above for two way types can be held now to a gas attaching part, generation efficiency improves.

[0023]

It is preferred that the check valve which operates with the pressure of the gas to generate is installed in the both ends of the gas attaching part of pipe shape so that the liquid fuel and gas in a tubular part may flow into one way. Thereby, liquid fuel circulates and the capacity factor of fuel improves.

[0024]

As construction material of a gas attaching part, although it can constitute from anticorrosion metals, such as synthetic resins, such as polytetrafluoroethylene, rigid polyvinyl chloride, polypropylene, and polyethylene, stainless steel, and nickel plate steel, for example, It is chemically stable in liquid fuel, and if it is the material which does not penetrate a gas, the kind in particular will not be limited.

[0025]

It is preferred that a water-repellent finish is given to the surface by the side of the gas attaching part of a negative electrode (liquid fuel side). When generating electricity using the hydrogen gas accumulated in the gas attaching part, it is because absorption of hydrogen to the hydrogen absorption material which is a negative electrode will take place promptly if it has given a water-repellent finish in the negative electrode surface.

[0026]

As for this water-repellent finish, it is preferred to be made by applying a fluoro-resin on the surface of a negative electrode. It is because the fluoro-resin is excellent in water repellence. As this fluoro-resin, for example Polytetrafluoroethylene, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, A tetrafluoroethylene hexafluoropropylene copolymer, a tetrafluoroethylene ethylenic copolymer,

polyvinylidene fluoride, polychlorotrifluoroethylene resin, etc. can be used.

[0027]

It is preferred that the catalyst provided with at least one function chosen as the surface by the side of the gas attaching part of a negative electrode (liquid fuel side) from the function which oxidizes the function and hydrogen which make hydrogen dissociate in the shape of an atom further is given. If the catalyst provided with the function to make hydrogen dissociate in the shape of an atom is given, absorption of hydrogen to a hydrogen absorption material can be promoted. If the catalyst provided with the function which oxidizes hydrogen is given, oxidation of hydrogen can be promoted and discharge with a negative electrode can be assisted. This catalyst may be made to contain in a negative electrode.

[0028]

The above-mentioned catalyst should just be provided with the function which oxidizes the function or hydrogen which makes hydrogen dissociate in the shape of an atom with the service temperature of a fuel cell, for example, metal, such as Pt, Pd, Rh, and nickel, can be used for it. Since especially Pt is excellent in the above-mentioned catalyst function also in this, it can use conveniently.

[0029]

As for this catalyst, being supported by porous carbon is preferred. By supporting a catalyst to porous carbon, it is because the surface area of the whole catalyst can be increased, the reaction surface product of hydrogen and a catalyst increases and dissociation of hydrogen or oxidation reaction can be promoted.

[0030]

The carrier which supports a catalyst has preferred carbon. When a catalyst oxidizes hydrogen, it is accompanied by an electronic transition, but it is because a reaction will advance smoothly if the carbon which has conductivity is used in that case.

[0031]

In order to oxidize the hydrogen generated to the gas attaching part, it is also effective to consider it as the gas diffusion electrode which has a function which oxidizes hydrogen in some negative electrodes. By making the hydrogen which was made to perform the decomposition reaction of metal hydride on the surface of the negative electrode containing a hydrogen absorption material, and was generated to the gas attaching part in the gas diffusion electrode oxidize, It is because the hydrogen efficiently generated to the gas attaching part can be consumed rather than forming the layer which has a function which oxidizes hydrogen on the surface of a negative electrode.

[0032]

The gas diffusion electrode includes the catalyst provided with the function which oxidizes the function or hydrogen which makes hydrogen dissociate in the shape of an atom. As the catalyst, metal, such as Pt, Pd, Rh, and nickel, can be used, for example. Since especially Pt is excellent in the above-

mentioned catalyst function also in this, it can use conveniently.

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As for this catalyst, being supported by porous carbon is preferred. By supporting a catalyst to porous carbon, it is because the surface area of the whole catalyst can be increased, the reaction surface product of hydrogen and a catalyst increases and dissociation of hydrogen gas or oxidation reaction can be promoted.

[0034]

The carrier which supports a catalyst has preferred carbon. When a catalyst oxidizes hydrogen, it is accompanied by an electronic transition, but it is because a reaction will advance smoothly if the carbon which has conductivity is used in that case.

[0035]

As for a gas diffusion electrode, it is preferred that a fluoro-resin is included. It is because the fluoro-resin is excellent in water repellence, so it can promote dissociation of hydrogen gas, or oxidation reaction. As this fluoro-resin, for example Polytetrafluoroethylene, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, A tetrafluoroethylene hexafluoropropylene copolymer, a tetrafluoroethylene ethylenic copolymer, polyvinylidene fluoride, polychlorotrifluoroethylene resin, etc. can be used.

[0036]

In order to separate the gas and liquid fuel by which the negative electrode reacted to liquid fuel and it was generated, it is also effective to arrange a gas liquid separation film at one which is connected with a gas attaching part or a gas attaching part of places. If a gas liquid separation film is especially arranged to the liquid fuel side of a gas diffusion electrode, in order only for the gas which the gas and liquid fuel by which it was generated dissociated and was emitted in the gas diffusion electrode to touch, the surface of a gas diffusion electrode does not get wet and high hydro acid-ized capability can be maintained.

[0037]

A gas liquid separation film is a film which can separate a gas and a fluid, and to liquid fuel, if chemically stable, it is good, but microporous polytetrafluoroethylene membrane is used suitably.

[0038]

As a hydrogen absorption material, a hydrogen storing metal alloy or a carbon nanotube is preferred. It is because these are excellent in the occlusion capacity of hydrogen.

[0039]

It is preferred that the solution which dissolved at least one chosen from the group which consists of KOH, NaOH, and LiOH as an electrolyte layer is included. It is because high ion conductivity can be given.

[0040]

As liquid fuel, the alkaline aqueous solution which dissolved metal hydride is preferred. It is because metal hydride can be stably saved in an alkaline aqueous solution. By touching the hydrogen absorption material which is a negative electrode as this metal hydride, what is necessary is just a compound in which a hydrolysis reaction occurs, and it is preferred that it is at least one chosen from the group which consists of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiAlH}_4$ ,  $\text{KH}$ , and  $\text{NaH}$  especially. It is because these can dissolve in water easily and there are many amounts of hydrogen supplies per unit mass.

[0041]

It is below the electromotive force 1.23V, and electromotive force is insufficient in one liquid fuel cell for driving many electronic equipment. By connecting two or more liquid fuel cells in series, and constituting a power plant, the electromotive force which can drive various electronic equipment is acquired.

[0042]

Since the power plant of high electromotive force is constituted, the liquid fuel cell of this invention, other power generation elements, for example, a fuel cell, a rechargeable battery, and a capacitor are also connectable in series. A power plant with a high energy density excellent in the high rate discharging characteristic can be constituted by connecting to a liquid fuel cell and parallel the capacitor or rechargeable battery which excelled the liquid fuel cell in the short-time high rate discharging characteristic.

[0043]

As a power generation element connected with a liquid fuel cell in series or in parallel, the fuel cell generated from hydrogen and oxygen is preferred. Since oxygen is contained in air, the special stores dept. for oxygen is unnecessary, only the electrode which returns oxygen should have it, and it serves as a cell with a high energy density. Hydrogen is a liquid fuel cell of this invention, and since it can use the hydrogen generated by the reaction of metal hydride and a hydrogen storing metal alloy, it does not need a new stores dept. for hydrogen other than the stores dept. for metal hydrides for liquid fuel cells.

[0044]

It is preferred to provide the lead pipe for leading hydrogen to the hydrogen pole part (negative-electrode part) of the fuel cell which uses hydrogen as fuel from the gas attaching part of a liquid fuel cell, when connecting with the liquid fuel cell of this invention the fuel cell which uses hydrogen as fuel in series or in parallel in the same power plant. It is because it becomes unnecessary to newly provide the hydrogen storage part for the fuel cell which uses hydrogen as fuel and a power plant can be miniaturized because this uses the hydrogen generated from the liquid fuel cell.

[0045]

By providing the gas attaching part which can collect and hold the gas generated from liquid fuel to the contact portion of the negative electrode of a liquid fuel cell, and liquid fuel, Generating of the



hydrogen which a negative electrode and liquid fuel react and is not used for power generation at the time of the power generation stop of a liquid fuel cell or low rate power generation will accumulate the hydrogen in a gas attaching part. This accumulated hydrogen is led to the hydrogen pole part of the fuel cell which uses other hydrogen as fuel with a lead pipe. If hydrogen is accumulated in this gas attaching part and a hydrogen pole part, contact with a negative electrode and liquid fuel will be intercepted by this accumulated hydrogen, and the reaction of a negative electrode and liquid fuel will stop. Useless consumption of liquid fuel can be controlled by this, and the energy density of a liquid fuel cell can be improved. When hydrogen of a hydrogen pole part and a gas attaching part is consumed at the time of usual power generation of a liquid fuel cell, liquid fuel newly flows into this gas attaching part from a liquid fuel stores dept. and a negative electrode and liquid fuel contact again, a negative electrode and liquid fuel react, hydrogen occurs, and power generation can be continued.

[0046]

It is also effective to provide a gas liquid separation film in the lead pipe for leading hydrogen to the hydrogen pole part of the fuel cell which uses hydrogen as fuel, and to separate liquid fuel and hydrogen. By supplying only hydrogen to a hydrogen pole part, it is because it can generate electricity stably.

[0047]

Next, an embodiment of the invention is described based on a drawing.

[0048]

## 20 (Embodiment 1)

Drawing 1 is a sectional view of the liquid fuel cell in Embodiment 1 of this invention. The anode 1 laminates the carbon layer 1b which becomes porous carbon powder from the end of carbon powder the catalyst was supported, for example, and the vapor-liquid-separation sheet 1a which consists of polytetrafluoroethylenes, and is constituted. The anode 1 has the function to return oxygen and can raise the performance by supporting a catalyst to porous carbon powder. Silver, platinum, a ruthenium, iridium oxide, a rare earth oxide, manganese oxide or silver, platinum, the alloy containing at least one ruthenium, etc. are used for the catalyst. In the carbon layer 1b of the anode 1, in order to give water repellence, polytetrafluoroethylene resin particles contain.

[0049]

The negative electrode 2a (hydrogen storing metal alloy pole) adheres to a conductive base, a hydrogen absorption material is formed, and it has a function which oxidizes fuel. As a hydrogen absorption material, carbon materials, such as a hydrogen storing metal alloy or a carbon nanotube, can be used, and especially the hydrogen storing metal alloy is suitable. Although the kind is not limited especially as the hydrogen storing metal alloy, For example,  $AB_5$  type hydrogen storing metal alloy represented with  $LaNi_5$ , The  $A_2B$  type hydrogen storing metal alloy of the magnesium system represented with  $AB_2$  type hydrogen storing metal alloy represented with  $ZnMn_2$  or its substitution

product, Mg<sub>2</sub>nickel, or its substitution product, a solid solution type vanadium system hydrogen storing metal alloy, etc. can be used. AB<sub>2</sub> type hydrogen storing metal alloy of a MmNi<sub>5</sub> system which replaced some nickel by Co etc. also in them using the misch metal (Mm) which is a mixture of a rare earth element is used especially suitably. It is because it excels in endurance and the capability of the occlusion and discharge of hydrogen.

[0050]

It consists of material which has corrosion resistance to an electrolyte as a conductive base of the negative electrode 2a, and what is necessary is just a base in which electric contact is acquired from a hydrogen absorption material, and the product made from nickel or the iron punching metals which carried out the nickel plate, a foam metal object, etc. are used.

[0051]

As a binder for sticking the hydrogen absorption material of the negative electrode 2a to a conductive base, it is chemically stable in an electrolyte, what is necessary is just the material which has adhesiveness, and polytetrafluoroethylene, latex, etc. can be used. Polytetrafluoroethylene is especially used suitably from giving water repellence to the negative electrode 2a.

[0052]

Negative-electrode 2b is the gas diffusion electrode provided with the function which oxidizes hydrogen electrochemically, and is arranged on the same flat surface as the negative electrode 2a. As this gas diffusion electrode, the thing of the same composition as the carbon layer 1b of the anode 1 can be used, and platinum particles etc. can be used as that catalyst, for example. The vapor-liquid-separation sheet 1a is installed in the field by the side of the liquid fuel of negative-electrode 2b. The negative electrode 2a and 2b are electrically connected in parallel.

[0053]

As an electrolyte of this embodiment, if liquefied, various things can be used, but especially an alkaline aqueous solution is used suitably. As this alkaline aqueous solution, what dissolved hydroxide of alkaline metals, such as KOH, NaOH, and LiOH, in 10 - 40 mass % grade water is preferred, and the mixed electrolyte containing hydroxide of two or more alkaline metals can also be used, for example.

[0054]

Since the above-mentioned electrolyte is held and an electrolyte layer is constituted, the separator 3 is arranged between the anode 1, the negative electrode 2a, and 2b. The nonwoven fabric which the kind in particular will not be limited if the construction material of the separator 3 is stable to an electrolyte, for example, consists of polypropylene, polyethylene, etc. is used. When using water for an electrolytic solvent, it is preferred to carry out hydrophilization treatment of the surface of the separator 3.

[0055]

Although metal hydride is used as a hydrogen supply source of the liquid fuel 4, As the metal hydride,  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{LiAlH}_4$ ,  $\text{NaAlH}_4$ ,  $\text{KAlH}_4$ ,  $\text{KH}$ ,  $\text{NaH}$ , etc. are used, and especially  $\text{NaBH}_4$  is used suitably, for example. It is because  $\text{NaBH}_4$  is more stable than other metal hydrides in water or an alkaline aqueous solution and a reaction with a hydrogen storing metal alloy is also moderate. The

5 metal hydride which is a hydrogen supply source can be used where a liquid electrolyte is dissolved or mixed.

[0056]

The anode 1, the separator 3 which constitutes an electrolyte layer, the negative electrode 2a, and 2b are sheet shaped shape, are laminated in order of the anode 1, the separator 3, the negative electrode

10 2a, and 2b, and constitute the electrode and the electrolyte integrated object, respectively.

[0057]

The fuel tank 5 in which the liquid fuel 4 is stored is adjoined and established in the negative electrode 2a, and the separator 3 and opposite hand of 2b. The fuel tank 5 comprises synthetic resins, such as polytetrafluoroethylene, rigid polyvinyl chloride, polypropylene, and polyethylene, and anticorrosion

15 metals, such as stainless steel, for example. However, to connect two or more cells in series and constitute a fuel cell module from a case where the fuel tank 5 is constituted from metal, it is necessary to cover the surface of the fuel tank 5 with an insulator so that each cells may not short-circuit electrically.

[0058]

The gas attaching part 6 which can collect and hold the gas generated from the liquid fuel 4 is formed in the contact portion of the negative electrode 2a, and 2b and the liquid fuel 4. The gas attaching part

20 6 of this embodiment is formed by the fuel tank 5 which is a liquid fuel stores dept., the negative electrode 2a, and the diaphragm 5a formed between 2bs. in the field by the side of the negative electrode of this diaphragm 5a, it is shown in drawing 2 -- the zigzag shape gutter [ like ] is formed.

25 The gas attaching part 6 forms the tubular part with this gutter, and the negative electrode 2a and 2b.

[0059]

The check valves 7a and 7b are installed in the both ends of the gas attaching part 6 so that the gas generated from the liquid fuel 4 and the liquid fuel 4 in the gas attaching part 6 may flow into one way. If the liquid fuel 4 and the negative electrode 2a in the gas attaching part 6 react and hydrogen

30 gas is emitted, the internal pressure in the gas attaching part 6 will rise, and the check valve 7a will be closed down. If hydrogen gas is emitted, the liquid fuel 4 in the gas attaching part 6 will be extruded to the check valve 7b side, and it will be filled with hydrogen gas by the inside of the gas attaching part 6. If power generation is begun, hydrogen gas in the gas attaching part 6 will oxidize with negative-electrode 2b (gas diffusion electrode). At this time, in the gas attaching part 6, since it will be in a

35 reduced pressure state, the check valve 7b is closed, and the liquid fuel 4 flows in the gas attaching part 6 from the check valve 7a. It circulates through the liquid fuel 4 in the gas attaching part 6 to one

way according to the above-mentioned structure.

[0060]

In order to perform efficiently the structure of circulation of the above-mentioned liquid fuel 4, the negative electrode 2a and 2b must be installed in this order to the flow direction of the liquid fuel 4 in the gas attaching part 6. By doing so, hydrogen gas in the gas attaching part 6 is consumed with negative-electrode 2b, and only the liquid fuel 4 can return from the check valve 7b to the fuel tank 5.

[0061]

As for the tube diameter of a tubular part, it is preferred to make it thin, 1-3 mm of a tube diameter is preferred, and its 1-2 mm is specifically more preferred so that the liquid fuel 4 and hydrogen gas in the above-mentioned gas attaching part 6 may be intermingled within a tubular part. If a tube diameter is enlarged, the liquid fuel 4 and hydrogen gas will interchange within a pipe, and the liquid fuel 4 will flow into the fuel cell installation surface side. On the other hand, if a tube diameter is made thin, it can be intermingled with surface tension, without the liquid fuel 4 and hydrogen gas interchanging with gravity. For this reason, the liquid fuel 4 and hydrogen gas come to flow into one way regardless of the direction of gravity by the above-mentioned circulation. Therefore, an installation direction is not limited but the fuel cell of this embodiment can be made position-free.

[0062]

The cover plate 8 is formed in the separator 3 and opposite hand of the anode 1, and the vent 9 is formed in the portion which touches the anode 1 of the cover plate 8. Thereby, oxygen in the atmosphere can touch the anode 1 through the vent 9.

[0063]

The charge collector 10 is connected to the anode 1 and the negative electrode 2a, and the charge collector 10 comprises the precious metals, such as platinum and gold, an anticorrosion metal which carried out nickel or a nickel plate, or carbon, for example.

[0064]

The fuel supply port 11 for supplying the liquid fuel 4 is established in the fuel tank 5. The liquid fuel 4 is supplied from the fuel supply port 11, and the fuel tank 5 is supplemented with it. When a fuel cell generates electricity, the fuel supply port 11 is sealed and the liquid fuel 4 is kept from leaking from a fuel cell.

[0065]

The vapor-liquid-separation hole 12a and the gas liquid separation film 12b are installed in fields other than the electrode surface the fuel tank 5 side. The gas liquid separation film 12b has a function which discharges only gas out of a tank, in order to prevent the internal pressure in the fuel tank 5 rising, and a tank exploding, when the hydrogen which was not consumed with the above-mentioned negative-electrode 2b (gas diffusion electrode) is discharged by the fuel tank 5.

[0066]

The sealant 13 made of rubber is arranged between the vapor-liquid-separation sheet 1a of the cover plate 8, and the fuel tank 5.

[0067]

**(Embodiment 2)**

5 Drawing 3 is a sectional view of the liquid fuel cell in Embodiment 2 of this invention. This embodiment is the structure which used the negative electrode of the liquid fuel cell of Embodiment 1 only as the negative electrode 2a (hydrogen storing metal alloy pole), newly formed the polymer electrolyte fuel cell 16, and led the gas attaching part 6 even to the polymer electrolyte fuel cell 16.

[0068]

10 The anode of the polymer electrolyte fuel cell 16 consists of the diffusion zone 15 and the positive electrode catalyst layer 17, and a negative electrode consists of the diffusion zone 15 and the negative-electrode catalyst bed 18. The solid polyelectrolyte membrane 14 is arranged between the positive electrode catalyst layer 17 and negative-electrode catalyst bed 18. The vapor-liquid-separation sheet 1a is arranged at the liquid fuel side of the negative-electrode catalyst bed 18. The polymer electrolyte  
15 fuel cell 16 is generated by the hydrogen generated at the reaction of the negative electrode 2a and the liquid fuel 4, and oxygen in the air. High voltage is obtained when this embodiment electrically connects 2 sets of anodes, and a negative electrode in series.

**EXAMPLE**

20 [0069]

Hereafter, this invention is concretely explained based on an example. However, this invention is not limited to the following examples.

[0070]

**(Example 1)**

25 The liquid fuel cell of the same structure as Embodiment 1 was produced as follows.

[0071]

The anode 1 was produced like next. After adding to the distilled water of 30-cm<sup>3</sup> and mixing and stirring carbon "BP-2000" (trade name) 0.25g which supported the platinum particles made from Cabot (CABOT) for 10 minutes, The aqueosity dispersion liquid 0.18g of the polytetrafluoroethylene of  
30 concentration 60 mass % were added, and it mixed and stirred for 20 more minutes. Then, n-butanol 8cm<sup>3</sup> was added, and it mixed and stirred for 20 minutes, and warmed at 200 more \*\*, and after mixing and stirring for 20 minutes, floc was made to sediment, the supernatant fluid was removed and anode catalyst paste was obtained. Apply the obtained paste to the nickel meshed plate electrode support of 40 meshes, dry, and it is considered as the carbon layer 1b, This was stuck to the "Gore-  
35 Tex" (trade name, 100-micrometer [ in thickness ], 50% of void content) film (vapor-liquid-separation sheet 1a) which is the Japan Gore-Tex polytetrafluoroethylene sheet by pressure by the pressure of

9MPa, and it was considered as the anode 1.

[0072]

The negative electrode 2a (hydrogen storing metal alloy pole) was produced as follows. Empirical formula:  $MmNi_{3.48}Co_{0.74}Mn_{0.4}Al_{0.3}$  (Mm) To the hydrogen storing metal alloy 100g which  
 5 consists of a misch metal which consists of La33 mass %, Ce47 mass %, Pr5 mass %, and Nd15 mass %. The aqueous dispersion liquid 1.3g of the Poly N-vinylacetamide solution 6g of 5 mass %, 0.1g of carboxymethyl cellulose, and latex of 50 mass % were added, it mixed, and the negative electrode mixture content paste was obtained. After having been applied and filled up with the obtained paste at the base which consists of nickel foam, drying and forming a negative electrode mixture layer,  
 10 pressing was carried out and it was considered as the negative electrode 2a.

[0073]

Negative-electrode 2b (gas diffusion electrode) was produced by the same method as an anode. However, the activated carbon (the rate of platinum particles and the platinum particles to the total mass of activated carbon is 5 mass %) which made platinum particles support instead of carbon was  
 15 used. Coverage of platinum was taken as 4 mg/cm<sup>2</sup>.

[0074]

As for liquid fuel, the electrolyte used the alkaline aqueous solution of NaBH<sub>4</sub> of 1.6 mass % using the nonwoven fabric of the product [ separator / 3 ] made from 120-micrometer-thick sulfonation polypropylene using the KOH solution of 30 mass %. The KOH solution of 29.5 mass % was used as  
 20 an alkaline aqueous solution.

[0075]

the gas attaching part 6 -- 2x2 mm of sections -- it was presupposed that it is tubular.

[0076]

#### (Example 2)

25 The liquid fuel cell of the same structure as Embodiment 2 was produced as follows.

[0077]

Instead of having arranged negative-electrode 2b (gas diffusion electrode) in the liquid fuel cell produced in Example 1, as shown in drawing 3, this example combined one piece and the one polymer electrolyte fuel cell 16, and produced the cell which used the whole negative electrode as the negative  
 30 electrode 2a (hydrogen storing metal alloy pole). The gas attaching part 6 of the liquid fuel cell connected with gas attaching part 6' of the polymer electrolyte fuel cell 16, as shown in drawing 3. It electrically connected in series and each liquid fuel cell and polymer electrolyte fuel cell 16 constituted the power plant.

[0078]

35 The polymer electrolyte fuel cell used by this example was produced as follows. "Ketchen black EC" (trade name) by lion Akzo 50 First, mass parts, The platinum support carbon which supported 50 mass

parts of platinum particles with a mean particle diameter of 3 nm Ten mass parts, the proton conductivity substance made from erection ROKEMU (Electrochem) "Nafion" (a trade name.) 10 Mass parts and five mass parts of water were prepared [ the solids concentration 5 mass % solution ] for the polytetrafluoroethylene emulsion solution by Daikin, LTD. "D1" (trade name and emulsion concentration 60 mass %) as 75 mass parts and a fluoro-resin binder. The homogenizer mixed and distributed these, and it applied and dried so that the amount of platinum might become  $0.3 \text{ mg/cm}^2$  to carbon crossing (diffusion zone 15). Next, heat pressing was performed for 2 minutes on condition of 120 \*\* and 10MPa, it fabricated as an electrode, and the positive electrode catalyst layer 17 and the negative-electrode catalyst bed 18 were obtained.

10 [0079]

Using Du Pont "Nafion 117" (trade name), the solid polyelectrolyte membrane 14 pinched this solid polyelectrolyte membrane 14 by the positive electrode catalyst layer 17 and the negative-electrode catalyst bed 18, and performed heat pressing for 3 minutes on condition of 120 \*\* and 10MPa.

[0080]

15 (Comparative example 1)

Drawing 4 is a sectional view of the conventional liquid fuel cell in the comparative example 1. This comparative example is the same composition as Example 1 except using the whole negative electrode as the negative electrode 2a (hydrogen storing metal alloy pole), and not having the gas attaching part and the vapor-liquid-separation hole, and having changed the installation direction of the cell. In this comparative example, since the liquid fuel 4 and the negative electrode 2a always touch, hydrogen gas will continue being emitted at the time of the power generation stop of a fuel cell, and some liquid fuel 4 will be consumed vainly.

[0081]

(Comparative example 2)

25 Drawing 5 is a sectional view of the conventional liquid fuel cell in the comparative example 2. It is the same composition as the comparative example 1 except having the vapor-liquid-separation hole 12a and the gas liquid separation film 12b for discharging the hydrogen gas emitted into the fuel tank 5 in this comparative example.

[0082]

30 Full restoration of the liquid fuel was carried out at each cell of Examples 1 and 2 and the comparative examples 1 and 2, and where between positive/negative terminals is made open, it observed. As a result, in the cell of Examples 1 and 2, generating of hydrogen gas stopped within 10 minutes after an observation start altogether. Generating of hydrogen gas continued, the pressure in a cell rose, the polytetrafluoroethylene sheet (vapor-liquid-separation sheet 1a) was damaged, and it stopped on the other hand, functioning as a cell by the cell of the comparative example 1. On the other hand, since the cell of the comparative example 2 formed the vapor-liquid-separation hole 12a and the gas liquid

35

separation film 12b, the pressure in a cell did not rise, but generating of hydrogen gas continued until all sodium borohydride in liquid fuel was hydrolyzed.

[0083]

Next, after discharging all used liquid fuel from each cell of Examples 1 and 2 and the comparative example 2, full restoration of the liquid fuel was newly carried out, constant current discharge was performed until cell voltage was set to 0.5V with the current density of 10 mA/cm<sup>2</sup>, and service capacity was measured. The result is shown in Table 1. The relative value when service capacity of Example 1 was made into 100% showed service capacity.

[0084]

## 10 TABLE 1

In Table 1, the thing with small service capacity of the comparative example 2 compared with Example 1 and Example 2, Since the gas attaching part is not provided in the comparative example 2, a constant rate of liquid fuel which is not related to the size of discharge current reacts to a negative electrode continuously, and since the hydrogen gas which was not used for the discharge reaction was emitted out of the cell, it thinks. On the other hand, since the gas attaching part is provided in Example 1 and Example 2, it is thought that liquid fuel has used efficiently the hydrogen gas which was not used for the discharge reaction from the negative electrode near the accumulation portion of hydrogen gas since hydrogen gas stopped emitting while it was accumulated into the cell.

[0085]

As for the thing with large service capacity of Example 2 compared with Example 1, since only the portion of a polymer electrolyte fuel cell of the volume of a gas attaching part is large compared with Example 1, Example 2 is considered because the reaction with the emitted hydrogen gas occurred efficiently.

## INDUSTRIAL APPLICABILITY

[0086]

In this invention, while inhibiting the reaction of the liquid fuel at the time of a power generation stop or low rate power generation, a liquid fuel cell with a high energy density can be provided by increasing absorption of hydrogen gas.

Therefore, miniaturization of the power supply of cordless apparatus, such as a laptop computer and a cellular phone, and high capacity-ization can be attained.

## BRIEF DESCRIPTION OF THE DRAWINGS



[0087]

[Drawing 1] It is a sectional view of the liquid fuel cell in Embodiment 1 of this invention.

[Drawing 2] It is a perspective view of the fuel tank of the liquid fuel cell in Embodiment 1 of this invention.

5 [Drawing 3] It is a sectional view of the liquid fuel cell in Embodiment 2 of this invention.

[Drawing 4] It is a sectional view of the conventional liquid fuel cell in the comparative example 1.

[Drawing 5] It is a sectional view of the conventional liquid fuel cell in the comparative example 2.

## DESCRIPTION OF NOTATIONS

10 [0088]

1 Anode

1a Vapor-liquid-separation sheet

1b Carbon layer

2a Negative electrode (hydrogen storing metal alloy pole)

15 2b Negative electrode (gas diffusion electrode)

3 Separator

4 Liquid fuel

5 Fuel tank

5a Diaphragm

20 6 Gas attaching part

6' gas attaching part

7a Check valve

7b Check valve

8 Cover plate

25 9 Vent

10 Charge collector

11 Fuel supply port

12a Vapor-liquid-separation hole

12b Gas liquid separation film

30 13 Sealant

14 Solid polyelectrolyte membrane

15 Diffusion zone

16 Polymer electrolyte fuel cell

17 Positive electrode catalyst layer

35 18 Negative-electrode catalyst bed

The present invention relates to

## CLAIMS

1. When said liquid fuel oxidizes with said negative electrode including an electrolyte layer arranged between an anode which returns oxygen, a negative electrode containing a  
5 hydrogen absorption material, and said anode and said negative electrode, and liquid fuel, it is a liquid fuel cell which a gas generates, a liquid fuel cell having an adjustment device which adjusts a reaction for which said liquid fuel oxidizes with said negative electrode according to power generation quantity of electricity using a gas generated from said liquid fuel.
2. The liquid fuel cell according to claim 1 provided with a gas attaching part which can  
10 hold a gas which said adjustment device generated from said liquid fuel so that a negative electrode may be touched.
3. The liquid fuel cell according to claim 2 arranged so that said liquid fuel and said negative electrode may not contact after said gas attaching part has held a gas generated from said liquid fuel.
- 15 4. The liquid fuel cell according to claim 2 or 3 with which said gas attaching part is provided with a tubular part, and said tubular part is installed towards two or more directions.
5. The liquid fuel cell according to any one of claims 1 to 4 which operates with a pressure which increases with a gas which said adjustment device generated from said liquid fuel.
- 20 6. The liquid fuel cell according to claim 4 or 5 further provided with a check valve for said tubular part to pass a gas generated from said liquid fuel and said liquid fuel only to one way.
7. The liquid fuel cell according to any one of claims 1 to 6 whose gas generated from said liquid fuel is hydrogen.
- 25 8. The liquid fuel cell according to any one of claims 1 to 7 with which a water-repellent finish is further given to the surface by the side of liquid fuel of said negative electrode.

9. The liquid fuel cell according to claim 8 currently made when said water-repellent finish applies a fluoro-resin to the surface of said negative electrode.

10. Said fluoro-resin Polytetrafluoroethylene, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, The liquid fuel cell according to claim 9 which is at least one chosen from a group which consists of a tetrafluoroethylene hexafluoropropylene copolymer, a  
5 tetrafluoroethylene ethylenic copolymer, polyvinylidene fluoride, and polychlorotrifluoroethylene resin.

11. The liquid fuel cell according to any one of claims 1 to 10 with which a catalyst provided with at least one function chosen as the surface by the side of liquid fuel of said  
10 negative electrode from a function which oxidizes a function and hydrogen which make hydrogen dissociate in the shape of an atom is given further.

12. The liquid fuel cell according to claim 11 with which said catalyst contains at least one element chosen from a group which consists of Pt, Pd, Rh, and nickel.

13. The liquid fuel cell according to claim 11 or 12 with which said catalyst is supported  
15 by porous carbon.

14. The liquid fuel cell according to any one of claims 1 to 13 which consists of a gas diffusion electrode in which said some of negative electrodes were provided with a function which oxidizes hydrogen.

15. The liquid fuel cell according to claim 14 with which said gas diffusion electrode  
20 contains at least one element chosen from a group which consists of Pt, Pd, Rh, and nickel.

16. The liquid fuel cell according to claim 15 with which said element is supported by porous carbon.

17. Said gas diffusion electrode Polytetrafluoroethylene, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer, A tetrafluoroethylene hexafluoropropylene copolymer, a tetrafluoroethylene ethylenic copolymer, The liquid fuel cell according to any one of claims  
25

14 to 16 containing at least one chosen from a group which consists of polyvinylidene fluoride and polychlorotrifluoroethylene resin.

18. The liquid fuel cell according to any one of claims 1 to 17 further provided with a gas liquid separation film for separating a gas generated from said liquid fuel, and said liquid fuel.

5 19. The liquid fuel cell according to claim 18 with which said gas liquid separation film consists of microporous polytetrafluoroethylene membrane.

20. A gap which wants to choose said hydrogen absorption material from a hydrogen storing metal alloy and a carbon nanotube, or the liquid fuel cell according to any one of claims 1 to 19 whose number is one.

10 21. The liquid fuel cell according to any one of claims 1 to 20 with which said electrolyte layer contains solution which dissolved at least one chosen from a group which consists of KOH, NaOH, and LiOH.

15 22. The liquid fuel cell according to any one of claims 1 to 21 with which said liquid fuel contains at least one chosen from a group which consists of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiAlH}_4$ ,  $\text{KH}$ , and  $\text{NaH}$ .

23. Two or more power generation elements are a gap to be chosen from series and parallel, or the power plant electrically connected by one side, A power plant, wherein at least one of said the power generation elements is the liquid fuel cell according to any one of claims 1 to 22.

20 24. The power plant according to claim 23 which is a fuel cell which power generation elements other than said liquid fuel cell generate from hydrogen and oxygen.

25 25. The power plant according to claim 23 or 24 further provided with a means to lead a gas to other fuel cells in the same power plant from said liquid fuel cell. A system for including